Method for determining ion exchange membrane resistance for electrodialysis systems

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HIGHLIGHTS

- A membrane resistance measurement system with platinum iridium wires is developed.
- Membrane resistance can be determined in a NaCl concentration range of 0.001–5 M.
- Reference electrodes' distance should be substantially larger than their diameter.

GRAPHICAL ABSTRACT
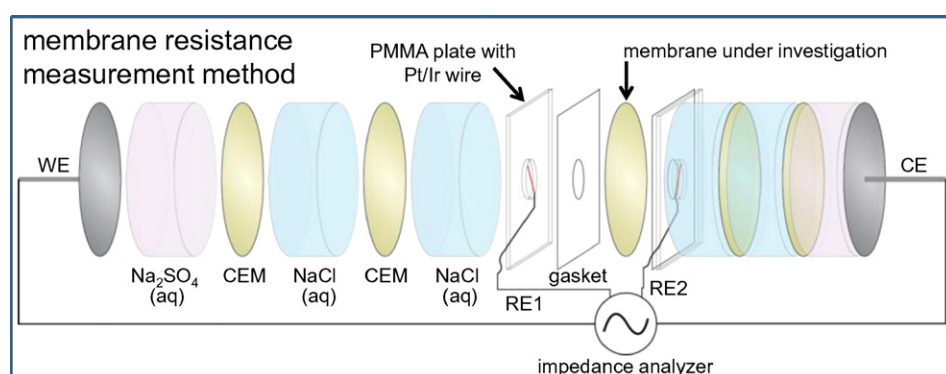
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ABSTRACT

Ion transport resistance is an important characteristic of ion exchange membranes. It is not a constant but is influenced by among other things the salt concentration in the external solution. A vast number of publications investigated the membrane resistance; however, the use of different methods leads to different results. Different approaches and possible flaws are discussed and a method for measuring membrane resistance is developed, evaluated, and described. It is shown that this method can be used in a wide concentration range of 0.001–5 M NaCl. The method is based on electrical impedance spectroscopy within an electrochemical cell containing four electrodes. An AC is applied on two work electrodes, while two thin platinum iridium wires are used as reference electrodes to evaluate the sample impedance. Membrane resistance is obtained from a differential impedance measurement of a solution without and with a membrane. Resistance of AMX and CMX membranes is determined.

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1. Introduction

Ion exchange membranes (IEMs) are used in many electrochemical processes where selective transport of charged particles is required. Whether used for instance in electrodialysis (ED), fuel cell technology, membrane capacitive deionization, or reversed electrodialysis; whenever a current is transported, low membrane resistance is energetically beneficial, because it allows for lower electrical losses or higher productivity. Resistance, R (Ω), is often described as the 'electrical resistance', which is defined as: the property of a conductor (i.e. resistor) to oppose the flow of the current, I (A), passing through the conductor when a potential, U (V), is applied across the conductor. When a salt solution is separated by IEMs, current is transported by ions present in this solution and by the ions in the membrane pores. Therefore, it might be

better to use the term ion transport resistance rather than electrical resistance in these kinds of application.

In liquids generally not the resistance, but its reciprocal representation; conductance, G (S), is used to describe the ability to transport current. The conductance, or conductivity, σ (S/m), of a solution is defined by the concentration and motilities of the charge carriers (ions, colloids) present [1]. For a simple solution, with only one salt present, the conductivity at defined temperature can therefore be used to determine the ion concentration. In practice the conductivity is determined by measuring the amount of current when a certain potential difference is applied over two defined electrodes. Just as solutions also the conductivity of membranes can be determined. In many previous investigations it was shown that membrane conductivity (i.e. membrane resistance) depends on the ion concentrations of the external solutions, e.g. [2–5]. A method for reliable determination of the membrane resistance under different circumstances can be very helpful to provide insight in e.g. energy consumption of an ED process, but also in the performance of the stack regarding the stagnant diffusion layers (SDLs). When the stack resistance due to the membranes (measured) and due to the ionic solutions between the membranes (calculated) is known this SDL resistance can be estimated [2]. When the SDL resistance is high there is likely no good flow distribution through the stack. An appealing method for investigation of the membrane conductance is electrical impedance spectroscopy (EIS) [6,7]. Currently there are several EIS based methods in use for the determination of membrane resistances.

The methodology of the membrane resistance measurement is shown to influence the measured result [8–10], as each method has its limitations or may include some erroneous parts in its approach, as will be discussed later on. In this work an EIS based method (frequency range 0.1–100 kHz) is defined for determining the ion transport resistance of IEMs in electrolyte solutions (e.g. NaCl 0.001–5 M).

2. Theory

2.1. Impedance measurements

The membrane's conductivity is determined by measuring its bulk membrane resistance R_m (Ω) against the flow of a direct current (DC) or an alternating current (AC) at controlled temperature. The conductivity σ is calculated through Eq. (1):

$$\sigma = \frac{\delta}{RA} \tag{1}$$

where δ corresponds to the distance between the electrodes (m) and A is the membrane cross-sectional area (m^2). The values of A and δ are system specific and R can be measured trough impedance measurements as shown later on. Eq. (1) is written for the real valued impedance, or resistance. The impedance Z (Ω) can be defined as a 'resistance' encountered when current flows through an electrochemical system and it describes in complex written form not only how well the system conducts electricity, but also in which amount it stores energy, either capacitive or inductive [7,11]. In experimental work it may be referred to as the frequency specific impedance of a material. The impedance is a complex number, defined to be the ratio of the complex potential and the complex current. The impedance can then be written as shown in Eq. (2) [6,7,12]:

$$Z = Z' + jZ'' \tag{2}$$

where Z' represents the real part of the impedance and jZ'' denotes the imaginary plane. During EIS measurements an alternating voltage (or alternating current) of known frequency (which is changed in time in a defined frequency range) and with defined amplitude is applied to an electrical or electrochemical system. The associated response (current or voltage) from the sample is measured. In a linear system the voltage response to a sinusoidal current signal is a sinusoid, at the same frequency. When the system has a complex-valued impedance, meaning that the imaginary value is not zero it will be shifted in phase ϕ. The phase is defined as the angle between the imaginary and real values plane as given in Eq. (3).

$$\phi = tan^{-1}\frac{Z''}{Z'} \tag{3}$$

If the phase between current and voltage is zero, this implies that there is no capacitive or inductive response of the system and that there is no imaginary part in the impedance. It is expected that the impedance of the IEM is real valued.

2.2. EIS and membranes

EIS is often used for characterizing electrode systems but it is also recognized that EIS is a very powerful method for analysis and characterization of (ion exchange) membranes in electrochemical systems [13–15], because the real part of the resistance can be distinguished from the total measured resistance and the measured spectrum can be used in modeling of the studied system. Although EIS is not a standard method in membrane characterization, a considerable number of publications on application of EIS in ion exchange membrane systems is present for instance refs. [2,3,8,9,14–28]. Nevertheless, there is no satisfying standard measurement method or procedure. In this work it is attempted to define a reliable and accurate method that may be used to determine the membrane resistance (R_M) of IEMs that are for example used in the (reversed) electrodialysis process. A correct and standardized method will improve the comparability of the membrane resistance measured in different experimental studies and leads to better understanding of the ion transport through IEMs.

In an experimental set-up for electrochemical measurements conductance measurements can be done with two, three, or four electrodes, which can be placed in various configurations as shown for example in refs. [7,9,14]. When there are two electrodes present one serves as counter electrode and reference electrode, while the other serves as working electrode and reference electrode [7]. A three electrode system includes the working electrode, the counter electrode and an additional reference electrode. In a three electrode system the potential difference between the reference electrode and working electrode is measured [7]. In the four electrode system two reference electrodes are used and no measurement has to be done on the current-generating electrodes [7]. The reference electrodes are connected to a high input impedance device, so that in principle current flow through these reference electrodes is avoided [7,20]. In this work the two and four electrode systems are considered, these are shown schematically in Fig. 1.

2.2.1. The two electrode method

An advantage of a two electrodes system is its robustness and simplicity. Within the measured signal of a two electrodes system lead resistance is included, which makes this system more suitable for measurements of samples where the lead impedance is very small compared to the sample impedance [19,20]. With two electrodes interfacial impedances may dominate the response in the frequency range ≤100 kHz [20]. At lower frequencies electrodes get polarized and show capacitive behavior, which can be observed in the higher value of the measured phase.

In two electrode systems the cell constant k_c (m^{-1}) is an important parameter. This k_c value reflects the ratio of distance and electrode area, $k_c = \delta/A_e$. When the distance δ (m) between two electrodes is increased, or the electrode area A_e (m^2) is decreased the impedance is increased, or conductivity is lowered. A set-up with a lower cell constant is more effective for measuring samples with high resistance [7]. Determining the (effective) electrode area might be difficult, due to its geometry and the so called fringe-field effect [29]. With a two electrode system conductivity measurements can be done by selecting the right electrode size,